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The acquired funding from ARO was efficiently used to set-up a pulsed laser deposition (PLD) facility at the NCAT campus. The PLD technique is one of the most popular and effective techniques used in the present days for the deposition of thin films. In this technique, a pulsed laser (usually an excimer) is directed on a solid target. The PLD facility at NCAT campus has added a new dimension to the various research and educational activities taking place at our campus under the umbrella of NSF Center for Advanced Materials and Smart Structures. We have carried out a number of important experiments using the PLD facility in NCAT campus. These experiments have resulted in several publications in peered reviewed journals. A list of these publications can be seen at http://camss.ncat.edu.

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A Final Performance Report

# A PULSED LASER DEPOSITION FACILITY FOR THE SYNTHESIS OF NOVEL SURFACE ENGINEERED AND ELECTRONIC CERAMIC MATERIALS

**Project number 4-41185**

**Submitted to**

**DOD-Air Force/AFOSR**
**Contract Number: F 49620–00–1-0366**

**by**

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## Executive Summary:

A fully operational pulsed laser deposition facility has been set-up at the North Carolina A & T State University campus. The present facility has enhanced tremendously the quality of both research and educational programs in Mechanical Engineering, Electrical Engineering, Physics and NSF Center for Advanced Materials and Smart Structures. Several faculties, research scientists and students at under graduate as well as graduate levels, have used the facility. A list of people who have used the facility very extensively is given below:

| Faculties: | Students: | |
|---|---|---|
| Dr. J. Sankar | S. Narela | Graduate (MS) |
| Dr. D. Kumar | Walter Gilomore | Graduate (Ph.D.) |
| Dr. S. Yarmolenko | Steve Coleman | Graduate (MS) |
| Dr. Clinton Lee | Cindy Waters | Graduate (Ph.D.) |
| Dr. D. Pai | Xinyu Wang | Graduate (Ph.D.) |

It is well known that the PLD technique is one of the most popular and effective techniques used in the present days for the deposition of thin films. We have carried out a number of important investigations using the PLD facility in NCAT campus. Some of the important publications and presentations coming out from these investigations are listed below. One of major areas of work, which has been accomplished using the PLD facility, is focused on: Synthesis of metal-ceramic thin film nanocomposites with improved mechanical properties. Under this task, we have fabricated thin films composite materials consisting of metallic nanocrystals embedded in an insulator host with significantly improved mechanical properties. The improvement in the hardness of $Al_2O_3$ thin films by embedding metal nanocrystals is related to the evolution of a microstructure, which impedes the manipulation and movement of dislocation and the growth of microcracks. The impedance in grain boundary movement is brought about by grain boundary hardening due to formation of well-separated metallic nanocrystallites in amorphous matrices.

## Publications:

1. Improved magnetic properties of self-assembled epitaxial nickel nanocrystallites in thin film ceramic matrix", Kumar D, Hue H, Nath TK, Kvit A, Narayan J, Sankar J., J. MATER. RES. **17**, APRIL 2002.
2. "Structural and magnetoresistance properties of $La_{2/3}Ca_{1/3}MnO_3$ thin films on buffered silicon substrates", Kumar D, Chattopadhyay S, Gilmore WM, Lee CB, Sankar J, Kvit AV, Sharma AK, Narayan J, Pietambaram SV and Singh RK , APPL. PHYS. LETT., **78**, 1098-1100, 2001.
3. "Magnetic properties of self-assembled nanoscale $La_{2/3}Ca_{1/3}MnO_3$ particles in alumina matrix", Katiyar P, Kumar D, Nath TK, Kvit AV, Narayan J, Chattopadhyay C, Gilmore WM, Coleman S, Clinton CB, Sankar J, and Singh RK, APPL. PHYS. LETT., **79**, 1327, 2001.

4. "Self-assembled epitaxial and polycrystalline magnetic nickel nanocrystallites", Kumar D, Zhou H, Nath TK, Kvit AV, Sankar J, and Narayan J, APPL. PHYS. LETT., **79**, $22^{nd}$ Oct.2001.
5. "Tunable properties of metal ceramic composite thin films", Kumar D, Narayan J, Nath TK, Sharma AK, Kvit A, Jin C, and Sankar J., SOLID STATE COMM., **119**, 63-66, 2001.
6. "High coercivity and superparamagnetic behavior of nanocrystalline iron particles in alumina matrix", Kumar D, Narayan J, Kvit AV, Sharma AK, Sankar J, J. MAG. MAG. MATER., **232**, 167, 2001.

**Presentations:**

1. "Nanoscale magnetic properties of self-assembled Ni and Fe particles in amorphous and crystalline matrices", European MRS Meeting, Strasbourg, France, June 18-21, 2002.
2. "Atomic level characterization of nickel crystallites of nanometer dimension", **R.7.12**, Symposium on Nanostructured interfaces, MRS Spring Meeting, April 204, 2002, San Francisco.
3. "Epitaxial growth of La-Sr-Mn-O thin films on buffered Si (100) substrate, **D 9.3**, Symposium on Perovskite Materials, MRS Spring Meeting, April 204, 2002, San Francisco.
4. "Tunable magnetic properties of nanoscale magnetic dots in ceramic matrix", Symposium P, MRS Fall Meeting, November 27-December 1, 2001, Boston.

## Introduction

The acquired funding from ARO was efficiently used to set-up a pulsed laser deposition (PLD) facility at the NCAT campus. The PLD technique is one of the most popular and effective techniques used in the present days for the deposition of thin films. In this technique, a pulsed laser (usually an excimer) is directed on a solid target. The 20-30 nanosecond laser pulse is focused to give an energy density (~ 1-10 J/ $cm^2$) sufficient to vaporize a few hundred angstroms of surface material (called the plume) in the form of neutral or ionic atoms and molecules with kinetic energies of a few eV, which then get deposited onto the substrate. The plasma temperature is high and the evaporants become more energetic when they pass through the plume. This affects the film deposition in a positive manner due to increase in the adatom surface mobility. The advantage of this process is the fast response, energetic evaporants and congruent evaporation. Use of short pulses helps to maintain high laser power density in a small area of the target and produces congruent evaporation. When the wavelength of the radiation is shorter, the absorption depth is shallower and hence splashing of particulates is decreased. Besides, by thermally heating the substrate, the surface mobility of the atoms reaching the substrate is increased and they can reach the thermodynamically favored lattice positions.

## A. Description of PLD Facility

The PLD facility at NCAT campus has added a new dimension to the various research and educational activities taking place at our campus under the umbrella of NSF Center for Advanced Materials and Smart Structures. Following is a list of equipments/automation packages, which were bought from Neocera Inc. using the grant money from AFOSR and cost sharing money from the Department of Mechanical Engineering and Department of Electrical Engineering at NCAT State University. The functions and features of those equipments/accessories also described below.

**Deposition chamber:** The deposition chamber combines a six-target carrousel and 2" substrate heater with 18" Chamber and variable height support frame to create a versatile multitarget pulsed laser vacuum deposition system. Some of the features of our deposition chamber are: Multi Target carrousel flange assembly, Substrate Heater Flange Assembly, Manual Gate/Throttle Valve, Support Frame, Stainless Steel Gas Manifold for one gas plus vent Convectron/Cold Cathode Vacuum Gauging, Programmable Substrate Controller, Oil-free 260 l/s or 520 l/s turbopump package. The photograph of our PLD system is shown in Fig. 1.

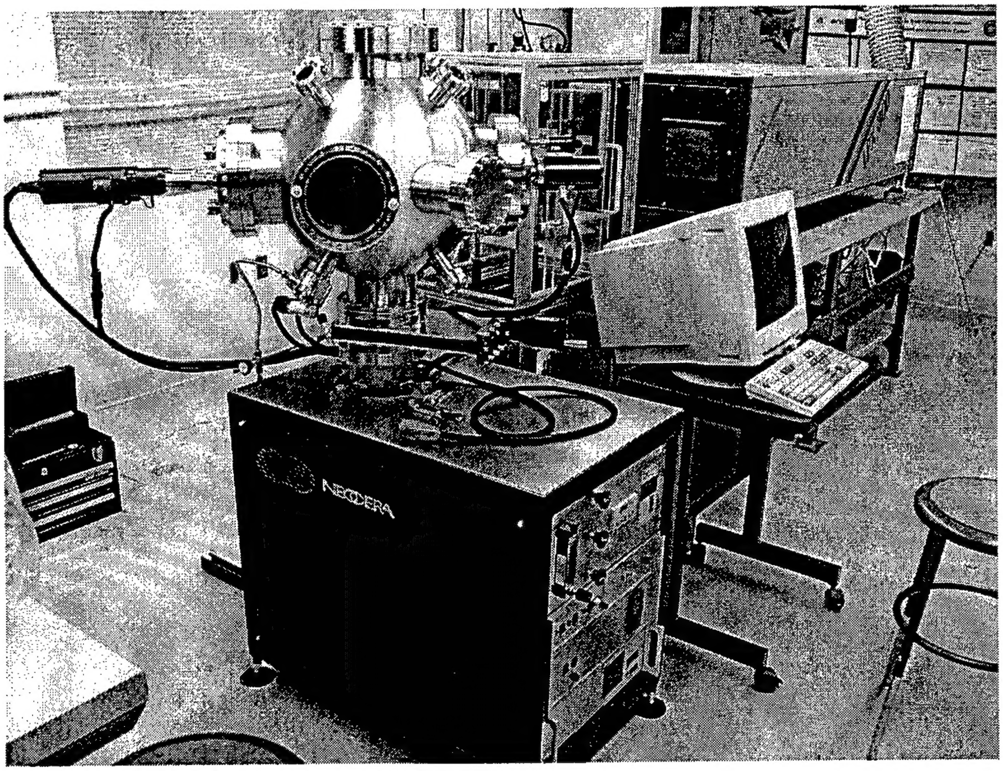


Fig. 1. Pulsed laser deposition system.

**Automated multitarget facility:** To make high-quality films by pulsed laser deposition, the target should move relative to the laser spot to conserve material and preserve the deposition geometry. Neocera's target holders accomplish this in several convenient ways. The simplest target holder spins a single target around its central axis, exposing a fresh surface to each pulse of the laser. The carrousels are designed to fabricate multilayer structures, or to deposit from multiple targets in rapid succession. The actual photograph of our automated multitarget carousel is shown in Fig. 2.

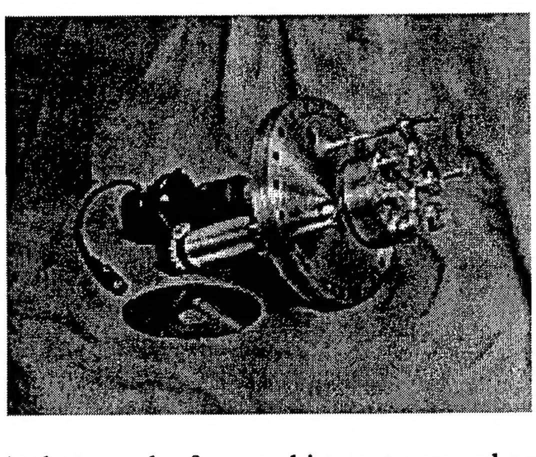

Fig. 2. A photograph of our multi-target carousel assembly.

The entire component is designed to fit through an 8" nipple (5.8" clearance diameter) without disassembly. The inside edge of a 1" target locates along the flange center line providing a compromise between 1" and 2" targets and beams focused near the center line of the flange. Targets rotate continuously at 17 rpm with the standard ac motor. The automation package is designed for ease of use and reliable operation. The carrousel platter rotates via a welded bellows feed through under the control of a DC servomotor. A computer coordinates the position of the platter with the triggering of the laser. The user defines a layer of deposited material by specifying the desired number of counts (thickness) and triggering frequency for a given target. The user then programs any sequence of layers and repetitions to create a multilayer thin film structure. Dwell times may also be included to allow the chamber to return to a steady-state condition before the next layer is deposited. Entire routines are quickly input, tested, stored, and recalled with the user-friendly Windows-based software package, which provides a PLD control panel displaying the current layer number, the number of times the routine has executed, the carrousel location in degrees, and the status of the deposition. The target also may be rastered over its diameter for improved target erosion uniformity. The Automated Target Carrousel can accommodate six 1" diameter targets or three 2" diameter targets. Target thickness can range from foils a few mils thick to disks up to 0.3" thick. Since the targets are bonded to the target mounts, perimeter shape is not critical; squares work as well as circles. Each target can be located reproducibly to the focal plane by adjusting the position of a target collar. Targets can be mounted and demounted without removing the carrousel from the chamber.

**Substrate heater:** Many materials require careful control of the substrate temperature during pulsed laser deposition. The heater bought from Neocera Inc. provides uniform heating of the substrate, and can operate at high temperatures in a range of environments, from vacuum to oxygen. The heater is mounted on flange as shown in Fig. 3. The flange includes an electrical feed through and shutter assembly, which allows us to pre-ablate the target surface without depositing material on the substrate.

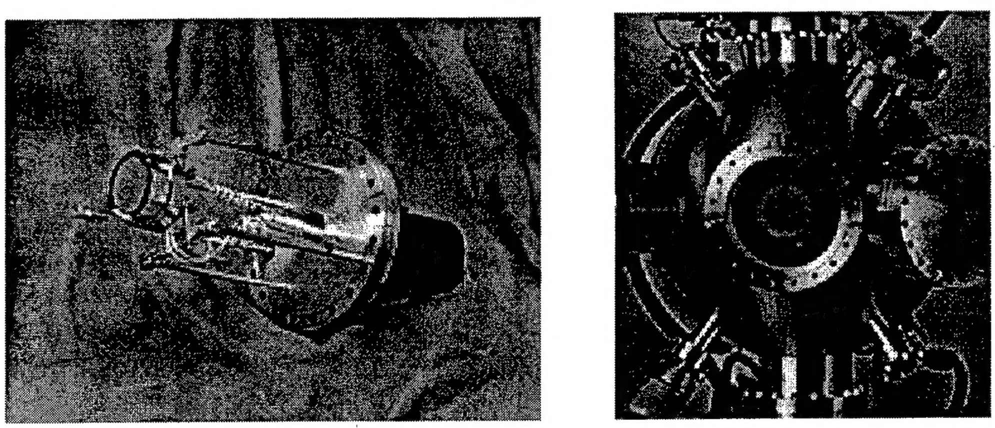

Fig. 3. Photographs of the substrate heater: (left) kept on a table top in cold condition (right) mounted in the deposition chamber and heated at 750 °C.

**LPX 305 Lambda Physik laser:** LPX 305 model is high duty cycle excimer laser, offering high repetition rates for scientific applications. A German Company named

Lambda Physik has manufactured it. The model combines proven design with state-of-the-art technology, setting new standards for reliability and performance. The laser works at 248 nm. The pulsed width is of the order of 20-30 nanoseconds. The repetition are can be varied from 1-50 Hz.

**Gas cabinet:** It is able to contain two reactive gas cylinders in it.

**Optical lenses and mirrors:** The mirror is reflective to 248 nm wavelength lights and lenses is be able to focus the beam down to as small spots as 0.5mm X 3mm.

**Enclosure of the laser beam:** The laser beam is passed through an enclosure made of a material of absorbing laser lights (248 nm). This is important from safety point of view.

## B. Technical accomplishment:

We have carried out a number of important experiments using the PLD facility in NCAT campus. These experiments have resulted in several publications in peered reviewed journals. A list of these publications is given in the executive summary. One of major areas of work which has been accomplished using the PLD facility in the NCAT campus is described in great details in the following section. This research was focused on: "Synthesis of metal-ceramic thin film nanocomposites with improved mechanical properties."

Composite materials consisting of metallic clusters or crystals of nanometric dimension embedded in an insulator host exhibit special optical, electrical, magnetic, and mechanical properties which have opened many possibilities of their use in various technological applications. (Stamm,1998; Lu,2000; Timp, 1999; Kumar, 2001; Prinz, 1998; Mehn, 1996; Katiyar, 2001; Ballesteros, 1997; Hirono, 2002; Veprek, 1999). For example, metal nanocrystals embedded in insulating materials offer enhanced mechanical properties, making them a promising candidate for use in machining tools. (Hirono, 2002; Veprek, 1999; Cselle, 1995; Rodeghiero, 1995; Sekino, 1997). The search for materials with enhanced hardness is driven by both the scientific curiosity of researchers to explore the possibilities of synthesizing a material whose hardness could approach or even exceed that of diamond and the technical importance of hard materials for wear protection of, e.g. machining tools. The importance of hard wear protective coatings for the machining applications is illustrated by the fact that today more than 40 % of all cutting tools are coated by wear resistant coatings and the market is growing fast. Wear resistant hard coatings for high speed dry machining would allow the industry to increase the productivity of expensive automated machines and to save on the high costs presently needed for environmentally hazardous coolant.

The metal nanocrystals embedded in insulating materials have been synthesized by quenching and heat treatments (Lu, 1991), sol-gel processes (De, 1996), sputtering (Liao, 1997), and ion implantation (Hertzberg, 1989). Most of these processes are multi-step processes, in which a post-deposition treatment is often needed to optimize the properties. However, these treatments can also alter the average grain size, size distribution, and spatial arrangement of the nanocrystals, with the possible unfavorable effects on the

mechanical properties of the nanocomposites. Unlike these methods, multiple target sequential pulsed laser deposition (PLD) permits independent control of synthesis of the nanocrystals and the embedding matrix. PLD has shown particular success in stoichiometric thin film deposition of complex oxides. Energetic (>100 eV) ions produced by ablation yield smooth, high-density films with good adhesion, especially desirable for mechanical applications. In this paper we report the fabrication of alternating-target PLD of Fe and Ni nanocrystals embedded in $Al_2O_3$ matrix. The nanocomposite exhibits superior mechanical properties with enhanced hardness and Young's modulus.

Nanocrystalline nickel and iron crystallites were embedded in alumina matrix using a KrF excimer laser (252 nm, 30 ns full width at half maximum) focused alternately onto high-purity targets of nickel or iron and alumina. The depositions were carried out on silicon substrates in a high vacuum environment (~5 X $10^{-7}$ Torr). The substrate temperature was approximately 500 °C. The energy density and repetition rate of the laser beam used were 2J/cm$^2$ and 10 Hz, respectively. The size distribution of metallic particles and the crystalline quality of both the matrix and metallic particles were investigated by cross-sectional scanning transmission electron microscopy with atomic number (Z) contrast (STEM-Z). Table 1 lists the hardness and particle size of nanocomposites produced using different metal deposition time.

Table 1. Hardness and particle size of nanocomposites produced using different metal deposition time.

| Deposition Time (s) | $Fe-Al_2O_3$ system | | $Ni-Al_2O_3$ system | |
|---|---|---|---|---|
| | Fe-size | Hardness (GPa) | Ni-size | Hardness (GPa) |
| 20 | 3 | 15 | 4 | 27.0 |
| 40 | 4.5 | 20 | 6 | 23.5 |
| 60 | 7 | 28 | 8 | 24.2 |
| 80 | 9 | 16 | 10.5 | 24.0 |

Shown in Fig. 4 is the variation of hardness of $Ni-Al_2O_3$ thin film composites as a function of the size of Ni particles embedded in $Al_2O_3$ matrix. For the sake of comparison, we have shown in the figure the hardness data of pure alumina film deposited under identical conditions. It is clear from the figure that the hardness of Ni-alumina composite is significantly higher than that of pure alumina films.

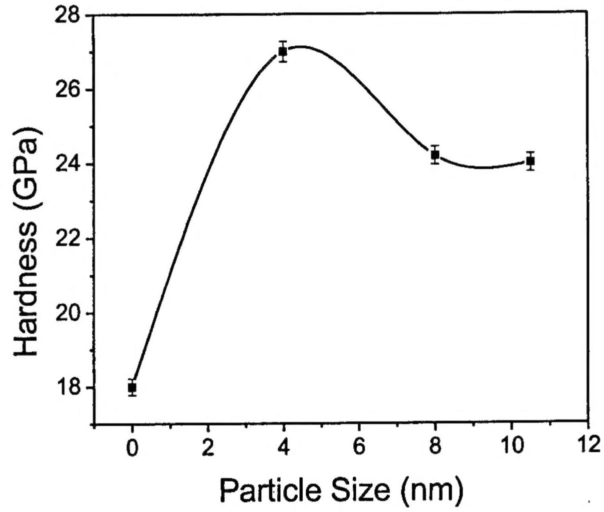


Fig. 4. Variation of hardness of Ni-$Al_2O_3$ thin film composites as a function of the size of Ni particles embedded in $Al_2O_3$ matrix.

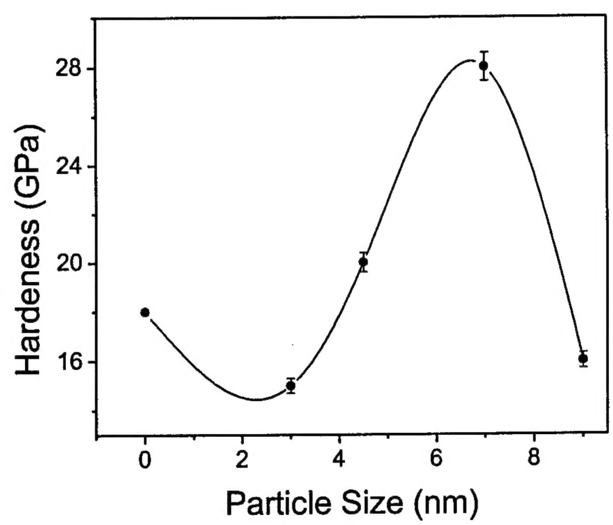


Fig. 5. Variation of hardness of Fe-$Al_2O_3$ thin film composites as a function of the size of Fe particles embedded in $Al_2O_3$ matrix.

However, a further increase in the particle size of embedded Ni particles resulted in the deterioration of hardness suggesting that there is an optimum size of metal particles, which imparts the composite the highest hardness. A supporting evidence in favor of this suggestion comes from our hardness measurements performed on a different thin film composite system consisted of Fe nanocrystals in alumina thin films. The results obtained are shown in Fig. 4.

According to the results presented in this figure, the hardness of first Fe- $Al_2O_3$ composite (size of Fe particles 3 nm) is in fact lower than that of pure alumina film.

However, the hardness of Fe- $Al_2O_3$ composite becomes more than that of pure alumina thin film when the size of the embedded Fe nanocrystals increases to 4.5 nm and the hardness reaches a peak at 7 nm, beyond which the hardness of the Fe- $Al_2O_3$ thin films composite (Fe particle size 9 nm) is again lower than that of pure alumina thin film.

The improvement in values of hardness of $Al_2O_3$ thin films by embedding metal nanocrystals is related to the evolution of a microstructure which efficiently hinders the manipulation and movement of dislocation and the growth of microcracks, which in turn, is achieved by grain boundary hardening described by Hall-Petch relationship (valid down to a crystallite size of 20-50 nm (Hertzberg, 1989; Hall, 1951):

$$\sigma_c = \sigma_0 + \frac{k_{gb}}{\sqrt{d}}$$

Here is $\sigma_c$ the critical fracture stress, $d$ the crystallite size, $\sigma_0$ and $k_{gb}$ are constants. With the crystallite size decreasing this limit, the fraction of the material in the grain boundaries increases which leads to a decrease in its strength and hardness due to an increase of grain boundary sliding (Siegel,1995; Siegel,1995; Hahn,1997; Yip, 1998; Schiotz, 1998). A simple phenomenological model has been used to describe the softening in terms of an increasing volume fraction of the grain boundary material $f_{gb}$ with the crystallite size decreasing below 1-6 nm :

$$H(f_{gb}) = (1 - f_{gb})H_c + f_{gb}H_{gb},$$

with $f_{gb}$ $\alpha$ $(1/d)$. Due to the flaws present, the hardness of grain boundary materials $h_{gb}$ is smaller than that of the crystallites $H_c$. Thus the average hardness of the material decreases with $d$ decreasing below 10 nm, an effect commonly known as reverse Hall-Petch effect. Recent computer simulation studies confirm that the reverse Hall-Petch dependence in nanocrystalline materials is due to the grain boundary sliding that occurs due to a large number of small sliding event of atomic plains at the grain boundaries without thermal activation, and therefore will ultimately impose a limit on how strong nanocrystalline metal may become (Chokshi, 1989; Nieman, 1991; Sanders, 1997). Although many details are still not understood, there is little doubt that grain boundary sliding is the reason for softening in this crystallite size range. Therefore, a further increase of the strength of hardness with decreasing crystallite size can be achieved only if grain boundary sliding is blocked by appropriate design of the material (Nieman, 1991; Sanders, 1997; Koehler, 1970). We have tried to achieve this condition by having a uniform distribution of isolated nanocrystals in an amorphous thin film matrix. In such situations, the grain boundaries formed at the interface are very strong and avoid or greatly reduce the grain boundary sliding. We believe that this is what primarily responsible for the realization of higher values of hardness for metal-alumina thin film composites consisted of isolated nanocrystalline metal particles (size below 10 nm) in amorphous matrices.

The improvement in the values of hardness of $Al_2O_3$ by embedding Ni and Fe nanoparticles may also be explained using the Koehler concept of mulitlayers for the design of strong solids. According to his concept, under applied stress a dislocation, which would form in softer layer (metal in the present study), would move toward the metal-ceramic interface, elastic strain in the second layer (alumina in the present study) with the higher elastic modulus would cause a repulsing force that would hinder the

dislocation from crossing that interface. Therefore, the hardness of Ni-$Al_2O_3$ and Fe-$Al_2O_3$ thin film composites, which are essentially multilayered structures costing of continuous layer of alumina thin films and discontinuous film of metals, is much larger than expected from the rule of mixture.

In summary, we have demonstrated the controlled fabrication of nanocrystals of pure metals and complex oxide materials of a few nanometers embedded in an insulating matrix using the PLD process. The structural characterizations carried have reveled that the particles are well separated from each other and the interfaces between the particle and the host matrix are free of oxide layers. The techniques used in the present investigation for sample preparation assumes significant importance in view of problems encountered in techniques commonly used to synthesize the nanoparticles. The improvement in the hardness of $Al_2O_3$ thin films by embedding metal nanocrystals is related to the evolution of a microstructure, which impedes the manipulation and movement of dislocation and the growth of microcracks. The impedance in grain boundary movement is brought about by grain boundary hardening due to formation of well-separated metallic nanocrystallites in amorphous matrices.

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